OBSERVATIONS ON THE RARE EARTHS: SOME ELECTROCHEMICAL STUDIES ON NON-AQUEOUS SOLUTIONS OF RARE EARTH METAL SALTS

BY

PAUL ALBERT ZIMMERMAN

A.B., Concordia Theological Seminary, 1941
B.D., Concordia Theological Seminary, 1944
A.M., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Even before the turn of the century chemists were interested in the role which non-aqueous solvents might be able to play as ionizing agents for inorganic compounds. They speculated that it might be possible to electrodeposit from non-aqueous solvents metals which cannot be deposited from aqueous solutions of their compounds. Thus, Lasynski in 1895 explored the usefulness of acetone and pyridine as ionizing solvents. He reported that he had been able to obtain metallic lithium by electrolyzing both acetone and pyridine solutions of lithium chloride (1). He was also able to electrodeposit metallic potassium from a solution of potassium chloride in acetone.

The pioneer work of Lasynski was extended in the years that followed by other chemists who were interested in the same problem. Many non-aqueous solvents were studied. Pyridine, liquid ammonia, and the alcohols received particular attention. In the middle thirties, a new class of solvents, the aliphatic amines, became available for the first time in fair amounts and at reasonable prices. Kobe and Putnam studied the ionizing properties of one of these amines, namely ethylenediamine (3). They found it to be comparable to liquid ammonia in its solvent properties and reported that they had been able to electrodeposit magnesium, lithium, sodium, and potassium from ethylenediamine. At about the same time, Dirkse and Briscoe reported that they had obtained metallic aluminum and magnesium by the electrolysis of monoethanolamine solutions of salts of these metals (2).

The work of Kobe and Putnam and of Dirkse and Briscoe suggested that it might prove fruitful to explore the possibility of using basic solvents as ionizing media for anhydrous rare earth metal salts. On theoretical grounds alone it seemed reasonable that anhydrous basic solvents would constitute excellent media for the electrodeposition of rare earth metals. Because of their basic nature, they provide a reducing environment conducive to the stabilization of low oxidation states. Accordingly, the present electrochemical investigation was undertaken in order to determine the properties of solutions of various anhydrous rare earth metal salts in basic solvents. Ethylenediamine, monoethanolamine, and morpholine were the solvents selected for study.

Materials And Apparatus

The ethylenediamine, monoethanolamine, and morpholine used in the investigation were obtained from Carbide and Carbon Chemicals Corporation. The rare earth materials were from the stock of the Division of Inorganic Chemistry at the University of Illinois. All other chemicals were of analytical reagent grade.

Conductance measurements were made by means of an Industrial Instruments Conductivity Bridge, Type RC. Absorption spectra were measured on the Beckman Spectrophotometer, Model DU.

Experimental

Information was obtained concerning solubilities of rare earth metal salts in ethylenediamine, monoethanolamine, and morpholine. Conductance measurements were made to establish the extent to which the salts studied ionized in these solvents. The possibility of electrodepositing rare earth metals from solutions of their salts in ethylenediamine and monoethanolamine was also explored. Neodymium bromide, neodymium iodide, neodymium acetate, yttrium iodide, yttrium acetate, and lanthanum nitrate were used in the in-

vestigation. They were prepared in the anhydrous state by high temperature reactions of rare earth metal oxides with the respective ammonium salts. The solvents also were dehydrated carefully prior to use. The starting materials were preserved in the anhydrous state by carrying out all experiments in an atmosphere of dry nitrogen.

Results

1. Solubility Studies

Rare earth metal salts were found to be moderately soluble both in monoethanolamine and in ethylenediamine, but only slightly soluble in morpholine. Lanthanum nitrate is exceptional in that it is moderately soluble in morpholine. Monoethanolamine was found to be a better solvent than ethylenediamine for all of the salts studied, except neodymium iodide.

Quantitative determinations showed the acetates of neodymium and yttrium to be much more soluble than the halides of these elements. The iodide of neodymium is more soluble than the bromide both in ethylenediamine and in morpholine. The solubility of lanthanum nitrate in ethylenediamine is approximately equal to that of neodymium iodide.

2. Conductance Studies

Conductance measurements showed ethanolamine to be superior to ethylenediamine as an ionizing solvent for weak electrolytes. This is to be attributed to the superior dielectric constant of ethanolamine. However, in the case of stronger electrolytes, particularly in more dilute solutions, ethylenediamine is superior to ethanolamine as an ionizing solvent. It was concluded that this latter phenomenon is to be attributed to the high viscosity of ethanolamine which acts to reduce the mobilities of ions in this solvent. Morpholine was found to be a poor ionizing agent for the rare earth metal salts studied.

The acetates were found to be poor electrolytes in the solvents studied. The nitrates, bromides, and iodides are fairly strong electrolytes.

The effect of the variation of temperature on the conductances of ethylenediamine, ethanolamine, and solutions of yttrium acetate in these solvents was studied. In every case, raising the temperature resulted in an increase in specific conductance. The addition of small amounts of water to ethylenediamine and to an ethylenediamine solution of yttrium acetate produced similar results.

3. Electrodeposition Studies

Smooth, thin, lustrous, metallic appearing plates, containing yttrium, neodymium, and lanthanum, respectively were obtained by the electrolysis of ethylenediamine solutions of the acetates, bromides, iodides, and nitrates. Platinum electrodes were used. The yttrium deposits varied in appearance from black to iron gray. The neodymium deposits were yellow in color. The lanthanum deposit was black.

Due to the high resistivities of the solutions, the plates obtained were of the order of from ten to thirty milligrams in weight. This circumstance made their characterization extremely difficult. However, they were found to be soluble in dilute hydrochloric acid, with the evolution of gas. The black yttrium deposits slowly turned white when exposed to water. The black lanthanum deposit turned gray on exposure to air. All of the deposits were shown to be potent reducing agents. Quantitative determinations of the reducing powers of the neodymium deposits were made, using potassium permanganate as an oxidizing agent. Microanalyses of the yttrium and neodymium plates indicated that they contained small amounts of carbon, hydrogen, and nitrogen. A study of the analytical data led to the conclusion that these elements had found their way into the deposits in the form of adsorbed solvent, absorbed moisture, and absorbed carbon dioxide.

X-ray diffraction patterns obtained from the yttrium deposit indicated it to be a crystalline material with high "d" spacings. The neodymium deposit was found to be on the borderline of very fine particle size and the amorphous state. The lan-

thanum deposit was indicated to be amorphous. However, it is possible that the lanthanum deposit originally contained a crystalline form of lanthanum metal which was subsequently converted to the amorphous oxide by the action of oxygen and moisture.

Polarographic studies produced inconclusive results due to experimental difficulties resident in the application of polarographic techniques to ethylenediamine solutions. However, there was some indication that the yttrium ion in ethylenediamine may be reduced electrolytically.

In short, the natures of the deposits did not permit it to be demonstrated conclusively that rare earth metals were electrodeposited from ethylenediamine. However, the properties of the deposits were characteristic of the rare earth metals. They constitute strong circumstantial evidence that the deposits contained rare earth metals. The deposits were contaminated, no doubt, by rare earth metal oxides and by adsorbed solvent.

No deposits were obtained by the electrolysis of ethanolamine solutions of rare earth metal salts. Morpholine solutions were not electrolyzed because of their extremely high resistivities.

BIBLIOGRAPHY

1. Audrieth, L. F. and Nelson, H. W.: Chem Rev., 8, 335 (1931).

2. Dirkse, T. P. and Briscoe, H. T.: Metal Ind., 36, 284 (1938).

3. Kobe, K. and Putnam, G. L.: Trans. Electrochem. Soc., 74, 609 (1938).

VITA

The author was born on June 25, 1918, in Danville, Illinois. He received his elementary education in Trinity Lutheran School of that city and was graduated from Danville High School in 1936. In 1939, he completed his pre-theological training at Concordia College, Fort Wayne, Indiana, and entered Concordia Theological Seminary, St. Louis, Missouri. He received the degree of Bachelor of Arts from Concordia Seminary in 1941 and continued his studies there the following year. The school year 1942-43 was spent by him as an instructor in science and religion at Bethany Lutheran College, Mankato, Minnesota. In 1944 he was graduated from Concordia Theological Seminary with the degree of Bachelor of Divinity. He was ordained into the Holy Ministry in the summer of 1944, after having accepted a call as professor of science and theology at Bethany Lutheran College, Mankato, Minnesota.

In 1947, the author received the degree of Master of Arts from the University of Illinois. During the summers of 1949 and 1950 he was a research assistant on the University of Illinois Rare Earth Research Program, sponsored by the Office of Naval Research. In the spring of 1950, Bethany Lutheran College granted him a leave of absence and a fellowship to permit the completion of the work for the doctorate in chemistry. He held an appointment as half-time teaching assistant in inorganic chemistry at the University of Illinois from September, 1950, to June, 1951.

The author is a member of Sigma Xi, Phi Lambda Upsilon, and the Association of Lutheran Secondary School Principals.